Electronic structure analysis of chemically delithiated $LiCoO_2$ using Electron Energy Loss Spectrometry

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$LiCoO_2$ is currently the preferred cathode material in secondary Li-ion batteries. Stoichiometric $LiCoO_2$ has rhombohedral symmetry and belongs to the $R\bar{3}m$ space group. This layered structure has Li and Co ions ordered along (111) planes to form alternating cation layers. The Co^{3+} ion, located in octahedral sites, forms a strong bond with neighboring oxygen atoms to produce O-Co-O sheets. Li^+ layers are sandwiched between these sheets of CoO_2.

We report an electronic structure analysis in samples of $Li_{1-x}CoO_2$ with x = 0.00, 0.08, 0.15, 0.35, 0.50, 0.75. These samples were chemically delithiated using an aqueous solution of potassium persulfate. Figure 1 shows the (003) and (104) x-ray diffraction peaks of $Li_{1-x}CoO_2$. There is a consistent shift in these peaks to smaller 2θ angles indicating an increase in the c lattice parameter attributed to the Li depletion. Electron energy loss spectrometry of the O *K*-edge and Co $L_{2,3}$-edge was used to probe the density of unoccupied states around the O and Co ions.

X-ray photoemission spectroscopy (XPS) and x-ray-absorption spectroscopy (XAS) have shown that $LiCoO_2$ is strongly covalent with available O 2*p* holes lying in the Co 3*d* band.[1] Transitions into these holes are observed in the near edge structure (530 eV) of the EELS spectra in Figure 2. This figure shows the O *K*-edge, normalized to the main peak at 542 eV, for the six samples. Figure 3 shows the white lines of the Co $L_{2,3}$-edge. These peaks are the result of transitions from the Co 2*p* into bound 3*d* states.

The most notable feature of these plots is the increased broadening and area of the O *K* near edge peak in the delithiated material. The corresponding increase in integrated intensity relative to the main peak at 540eV (I_{pre}/I_{main}) is shown in Figure 2. The pre-peak growth between $Li_{1.0}CoO_2$ and $Li_{0.5}CoO_2$ is approximately 18% and is indicative of a significant increase in the unoccupied O 2*p* states. As Li is depleted, there is a corresponding decrease in the charge density surrounding the O ion evolving the Co-O bonding towards a more ionic character. Conversely, The Co $L_{2,3}$-edge shown in Figure 3 reveals little variation between the lithiated and delithiated regions.

It is our contention that the net occupancy of the Co valence is virtually unaffected by Li concentration. It is the unoccupied Co-O antibonding states, evident in EELS as holes in the O 2*p* states, that are responsible for accommodating the incoming Li 2*s* electron. Such a model for charge compensation is supported by computational work done by Aydinol *et al.*[2] This study showed that during Li intercalation, the incoming electronic charge is almost entirely accommodated by the O ions. It also revealed a significant rearrangement, but little net charge compensation, around the Co ions.

References

[1] J. van Elp *et al.*, *Phys. Rev. B* **44**, 6090 (1991)
[2] M. Aydinol *et al.*, *Phys. Rev. B* **56**, 1354 (1997)

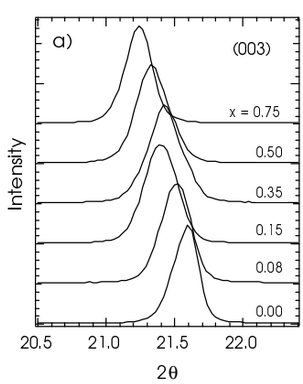
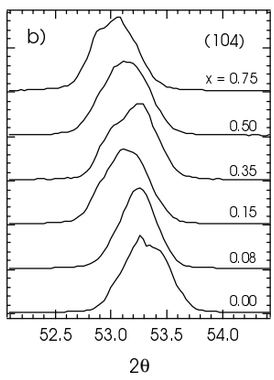


Fig. 1 a) (003) and b) (104) x-ray diffraction peaks of $Li_{1-x}CoO_2$ using Co*K*α radiation



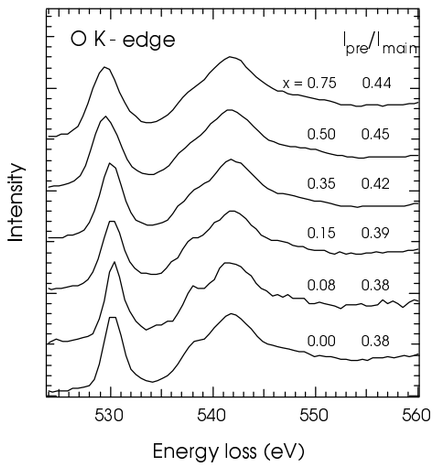


Fig. 2 EELS spectra of the O *K*-edge from $Li_{1-x}CoO_2$. Ratios of integrated intensities of the pre-peak (526-534eV) to the main peak (534-545eV) are shown.

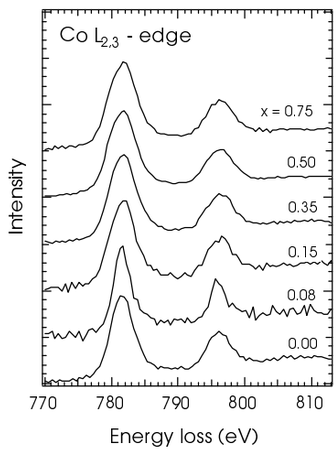


Fig 3 Co $L_{2,3}$-edge from $Li_{1-x}CoO_2$